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(54) Title: DIRECT SYNTHESIS BY LIVING CATIONIC POLYMERIZATION OF NITROGEN-CONTAINING POLYMERS			
(57) Abstract <p>A method is provided for the direct synthesis by living cationic polymerization of novel polymeric materials functionalized with nitrogen-containing functional groups such as terminal azido, cyano, carbonylamino, cyanato, thiocyanato or thiocarbonylamino groups. Polymerization and functionalization occur in a substantially simultaneous manner. All necessary reactants for the functionalization are present when polymerization is initiated. The nitrogen-containing functional group is provided as a part of a molecule having a release moiety which is preferably resonance stabilized or a tertiary alkyl type and which acts to aid the nitrogen-containing species in functioning as a leaving group.</p>			

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DIRECT SYNTHESIS BY LIVING CATIONIC
POLYMERIZATION OF NITROGEN-CONTAINING POLYMERS

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BACKGROUND OF THE INVENTION

Field of the Invention

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This invention relates to a method for direct synthesis, by living cationic polymerization, of nitrogen-containing polymers, and particularly to the production of nitrogen-containing polymeric materials in a single step Friedel-Crafts polymerization of olefinic materials containing substantial amounts of isobutylene.

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Description of Related Art

A review of carbocationic macromolecular engineering is provided in Kennedy and Ivan, Designed Polymers by Carbocationic Molecular Engineering: Theory and Practice, Hanser Publishers, Munich, Vienna, New York and Barcelona. Living polymerizations are defined (page 32) as ideal living polymerization in which charge transfer and termination are absent, and quasi-living polymerizations as having rapidly reversible charge transfer and/or termination present wherein the rate of these processes is faster than that of propagation. In either case the living behavior of the polymer results in a polymer in which charge transfer and termination are absent.

25 For the purpose of the present invention, living polymers are therefore defined as polymers which have substantially and preferably no apparent chain transfer and termination. Resulting polymers have low polydispersity indices (molecular weight distributions) of preferably less than 1.5 and in the range of 1.5 to the ideal value of 1, where all of the molecular chains are of the same length. Cationic living

30 polymerization systems take place by the polymerization reaction of monomers in the presence of a cationic initiator. A living polymerization system is one wherein the molar ratio of the monomer to initiator is equal to the degree of polymerization. The calculated molecular weight, therefore, equals the degree of polymerization times the molecular weight of the monomer plus the molecular weight of the initiator. Ideally, in

35 a living system, the measured number average molecular weight is equal to the calculated molecular weight, evidencing the absence of true termination.

Polymers, particularly polyolefin substrates, having nitrogen-containing functional groups such as the azide, cyano, carbonylamino or thiocarbonylamino groups are useful since the functional group is polar, and imparts desirable properties

to a polyolefinic substrate. Also, these groups may act as a reactive site for further modification of the polymer. Nitrogen-containing polyisobutylenes have applications such as lube additives, compatibilizers, emulsifiers, and the like. For example, azide terminal polymers may be further modified by phthalamidation or reduction of the azide group producing useful polymer products. For instance, reduction of the azide group of polyisobutylenes and addition of a polar moiety to the alpha nitrogen atom may result in improved polymeric compatibilizers, emulsifiers, etc. Prior art processes for synthesis of polymers having nitrogen-containing functional groups, such as nitrogen-containing polyisobutylene, involve several reaction steps. Chain end functionalization is known in the field of cationic polymerization.

The art further discloses that it could be possible to achieve direct functionalization by cationic polymerization of polymers end-capped by nitrogen containing functions using, for instance, an initiator having a pseudohalogen function of the benzylic type. Pseudohalogen or halogenoids include inorganic anions, e.g., CN^- , CNO^- , CNS^- and N_3 which have properties resembling those of halide ions as disclosed in Discher, Modern Inorganic Pharmaceutical Chemistry, John Wiley & Sons, Inc., N.Y., p. 343 (1964). In a single chemical process a polymer is derived from the monomer, using an initiator having nitrogen-containing function such as azide, cyano, carbonylamino or thiocarbonylamino group. Results such as these are referred to in U.S. Patent No. 5,032,653. However, the polymeric products were not disclosed to have a narrow molecular distribution (i.e., monodispersed type). The molecular weight was controlled by the monomer feed rate and the amount of Lewis acid catalyst as well as the monomer to initiator ratio. The amount of initiator was based on a Lewis acid to initiator mole ratio of 3:1 to 1:3 with enhanced results as the ratio approaches 1:1. The molecular weight distribution (MWD) is controlled based on monomer feed rate and product removal rate.

There are three different and desirable goals for synthesis of polymers by cationic polymerization as taught herein: (1) specific functionalization of the chain ends by a nitrogen-containing function, using direct synthesis from the monomer and the initiator which is incorporated in the resulting polymer; (2) easy control of the molecular weight by adjustment of the monomer to initiator ratios and low polydispersity index, (low MWD); and (3) control of molecular weight and MWD in the absence of molecular weight control additive(s).

SUMMARY OF THE INVENTION

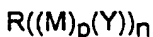
A method for the direct synthesis of polymeric materials functionalized with nitrogen-containing functional groups, comprising the steps of providing a cationically polymerizable monomer, and initiating polymerization by the addition of a cationic

polymerization catalyst, in the presence of a nitrogen-containing initiator compound having at least one nitrogen-containing functional group selected from -N₃, -NCO, -OCN, -SCN, -CN and -NCS chemically bound to a release moiety, wherein the ratio of moles of catalyst to nitrogen-containing functional groups is greater than 3:1. The
 5 resulting polymer is terminally substituted by the nitrogen-containing functional groups. The present invention includes preferred initiator bis(1-azido-1-methylethyl)benzene and the method to prepare such preferred initiator.

In other preferred embodiments, the nitrogen-containing functional group is bound to a secondary or tertiary carbon atom of the release moiety. Preferred
 10 nitrogen-containing initiators include hydrocarbyl compounds and silyl compounds, substituted with at least one nitrogen-containing group comprising azido (-N₃), cyano (also referred to as nitrile) (-CN), isocyanato (carbonylamino) (-NCO), thiocarbonylamino (isothiocyanato) (-NCS), cyanato (-OCN), and thiocyanato (-SCN). In certain preferred embodiments the polymerization catalyst is a Friedel-Crafts
 15 catalyst and the nitrogen-containing initiator and monomer are preferably admixed in the substantial absence of the Friedel-Crafts catalyst.

The process of the present invention is a "living polymerization". The living polymer is achieved by polymerizing the monomer with a catalyst to initiator ratio of greater than 3.0:1; a most useful range of from 3.1:1 to 30:1, and more specifically
 20 4:1 to 30:1 and 6:1 to 20:1. This results in a polymer with a narrow molecular weight distribution (MWD) ($\overline{M}_w/\overline{M}_n$) also referred to as a low dispersity, preferably less than 1.5, more preferably less than 1.4, and typically ranging from 1.2 to 1.3. This is obtained directly from polymerization without resort to additional steps to separate polymers at different molecular weights. The polymer made by the claimed process
 25 has as a terminal group the nitrogen-containing functional group. The molecular weight can be varied and can range from 300 or lower to 15,000,000 or higher with a specific range of from 300 to 15,000,000 and preferred ranges depending upon use. An advantage of the polymerization method of the present invention is that the functionalization is obtained directly from the mixture of monomer, initiator, Lewis acid
 30 and solvent without the need of other functionalization effecting compounds such as electron donor type compounds disclosed in the art. The resulting polymer is characterized by the advantages of a high specificity of functionalization combined with a narrower molecular weight distribution. Additionally, the method of the present invention enables easy control over the desirable molecular weight by adjusting the
 35 initial monomer to initiator a concentration ratio without the need of an electron donor.

The present invention includes a polymer composition having the formula:



R is selected from at least one group consisting of H, a hydrocarbyl group, and a hydrocarbyl-substituted silyl group. R can be alkyl, aryl, alkylaryl and arylalkyl. Y is selected from at least one group consisting of an azido, cyano, carbonylamino, thiocarbonylamino, cyanato and thiocyanato; a preferred Y is an azido group. M is at least one repeat unit derived from a cationically polymerizable monomer; useful monomers include straight and branched chain alpha-olefins, isoolefins, alicyclic monoolefins, cycloaliphatic compounds, styrene derivatives, indene and derivatives thereof, and other monoolefins and heterocyclic monomers. p is an integer greater than 1 and preferably sufficient to attain a desired molecular weight. n is an integer of at least 1, preferably 1 to 10 and most preferably 1 to 2.

Where the initiator has more than one functional group the polymer can have the plurality of arms ranging from 2 to 10 or more. This type of polymer is considered a "star polymer", but advantageously one in which each arm is substantially equal in length due to the narrow MWD. The nitrogen containing end groups can be reacted to form a desired functional terminal group including amines to prepare new telechelic oligomers. Uses include lubricant dispersants, viscosity improvers, synthetic lubricating oils, and thermoplastic elastomers.

20 DETAILED DESCRIPTION

As will be illustrated from the preferred embodiment, the present invention provides a way to obtain, at the same time, complete functionalization of the polymer by a monofunctional pseudohalogen or halogenoid initiator by direct synthesis using living cationic polymerization. When using a monofunctional initiator, the polymer product has a functionality of up to, and preferably, 1. When using a bifunctional initiator, the polymer product has a functionality of up to, and preferably, 2. The polymer has a narrow molecular weight distribution (MWD), or a low polydispersity index, as measured by weight average molecular weight divided by number average molecular weight. The MWD should ideally be 1.0, preferably less than 1.5, preferably from 1.0 up to 1.5, more preferably 1.0 to 1.4, with preferred values typically at 1.1 to 1.4. Preferred polymers produced in accordance with the method of the present invention are telechelic polymers. The functional groups are derived from the initiator with at least one functional group preferably containing nitrogen. In the living polymerization process using an initiator having one functional nitrogen-containing group, the functionality of the polymer is close to the theoretical value of 1, and typically greater than 0.7. Where the initiator contains more than one pseudohalide function the functionality would be expected to be close to a multiple of

the number of functional groups. For example, an initiator containing two pseudohalide functional groups would be expected to have a functionality of greater than 1.4 and preferably close to 2.

The foregoing and other aspects of the invention are provided by a living cationic polymerization process comprising polymerization of a monomer in the presence of an initiator and a catalyst, preferably in a solvent under conditions which result in living polymerization.

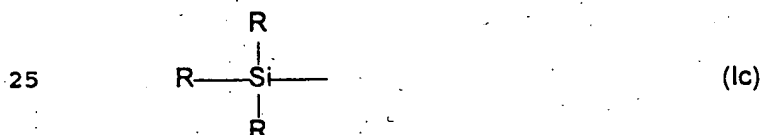
The nitrogen-containing compound employed as initiator in this invention comprises at least one member selected from the group consisting of (i) compounds of the formula:



wherein R is hydrogen or a hydrocarbyl group, n is a positive integer, preferably an integer of from 1 to 10, more preferably 1 or 2 and Y is $-N_3$, $-CN$, $-NCO$, $-OC\equiv N$, $-SC\equiv N$; or $-NCS$; and (ii) compounds of the formula:



wherein n and Y are as defined above, and R^* comprises a hydrocarbyl-substituted silyl group of the formula:



wherein each R is the same or different and is hydrocarbyl.

Exemplary of hydrocarbyl R groups are alkyl of from 3 to 100 carbon atoms, preferably 4 to 20 carbon atoms, aryl of from 6 to 20 carbon atoms, preferably from 6 to 15 carbon atoms, alkaryl and aralkyl of from 7 to 100 carbon atoms (e.g., 7 to 20 carbon atoms), and cycloaliphatic of from 3 to 20 carbon atoms, preferably from 3 to 12 carbon atoms. When n is 1, R in Formula (1a) generally comprise an alkyl group of from 3 to 12 carbon atoms, preferably from 3 to 20 carbon atoms, such as propyl, butyl, pentyl, octyl, decyl, dodecyl, and the like, and can be a polymeric group.

Most preferably R in Formula (1a) comprises a moiety of the formula:



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wherein R^1 , R^2 and R^3 are the same or different and are H or hydrocarbyl (e.g., alkyl, aryl, alkaryl, aralkyl, heterocyclic or cycloalkyl) with the proviso that at least two of R^1 , R^2 , and R^3 are hydrocarbyl; most preferably all of R^1 , R^2 and R^3 are hydrocarbyl. Exemplary of such secondary and tertiary alkyl groups are isopropyl, tert-butyl, 1-methylpropyl, 1-ethylbutyl, 1,2-dimethylbutyl, and the like. Exemplary of such alkaryl R^1 , R^2 or R^3 groups are ϕCH_2 -, $\text{CH}_3\phi\text{CH}_2$ -, $-\phi\text{C}_2\text{H}_5$ and the like. Further examples of such R^1 , R^2 or R^3 groups are $\text{CH}_3\phi$ -, $(\text{CH}_3)_2\phi$ - and the like. The carbonylamino (-NCO) and thiocarbonylamino (-NCS) substituted compounds are isocyanates and isothiocyanates, respectively.

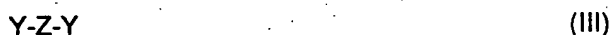
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It will be understood that the hydrocarbyl-substituted nitrogen-containing initiators of Formula (Ia) can comprise a polymer, having one or more Y-functional groups which can be added by grafting. Useful polymers are, for example, a polyalkene, such as a C_2 to C_{10} monoolefin homopolymer or a copolymer (e.g., polyisobutylene, ethylene-propylene copolymer), polydiene, such as hydrogenated or nonhydrogenated polyisoprene, polybutadiene and isoprene-butadiene, and aromatic-containing polymers (e.g., styrene-isoprene, styrene-butadiene, methylstyrene-isoprene-butadiene polymers), and ethylene-propylene-conjugated diene terpolymer.

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Useful nitrogen-containing initiators include disubstituted compounds of the formula:

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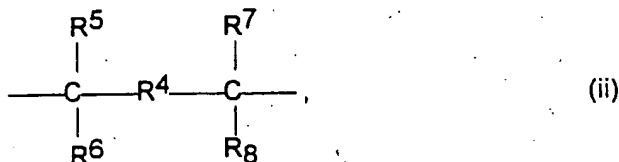


wherein Y is as defined above, and Z comprises a

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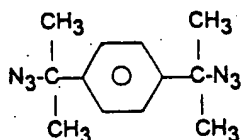


group wherein R^5 , R^6 , R^7 and R^8 are the same or different and comprise H or hydrocarbyl, e.g., alkyl of from 1 to 100 carbon atoms (e.g., methyl, ethyl, isopropyl,

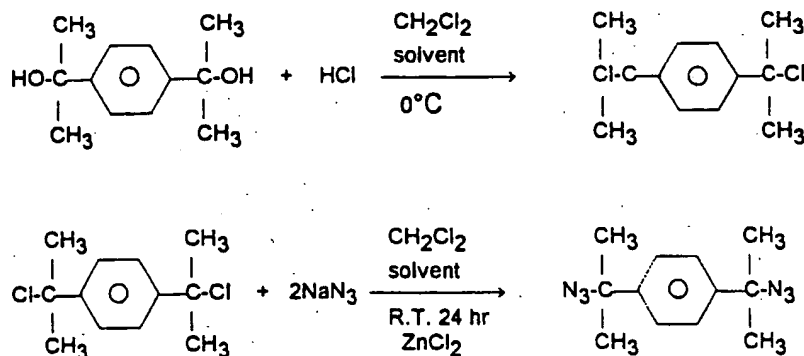
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butyl and the like), cycloalkyl of from 3 to 10 carbon atoms (e.g., cyclohexyl, cyclobutyl and the like), aryl of from 6 to 20 carbon atoms (e.g., phenyl, naphthyl and the like), or aralkyl and alkaryl of from 7 to 20 carbon atoms (e.g., tolyl, cresyl, xylyl, benzyl, ethylbenzyl and the like), and R^4 comprises $-(CH_2)_a-$ or $-Ar-$, wherein a is an integer of from 3 to 20, and preferably 3 to 10, and wherein Ar is an arylene group of from 6 to 20 carbon atoms, or aryl-substituted arylene, e.g., C_1 to C_{20} (preferably C_1 to C_{10}) alkyl mono- or disubstituted arylene group of from 7 to 40 carbon atoms (e.g., phenylene, naphthylene, mono- or dialkyl substituted derivatives of the foregoing, and the like).

A preferred initiator of the present invention, particularly for making linear living polymer, is bis(1-azido-1-methylethyl)benzene having the formula:

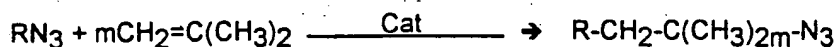


The bis(1-azido-1-methylethyl)benzene can be prepared by reacting dicumyl alcohol with a halogen containing compound to form dicumyl halide. The dicumyl halide is reacted with an azide containing compound to form the bis(1-azido-1-methylethyl)benzene. The halogen-containing compound is preferably a bromide or chloride and more preferably HCl, and the azide containing compound is preferably NaN_3 . The reactions can be conducted in the presence of suitable solvents under suitable conditions. The dicumyl alcohol can be reacted with HCl in a polar solvent such as methane dichloride under reflux conditions. The dicumyl chloride can be reacted with sodium azide in a solvent under reflux conditions, preferably with a weak Lewis acid catalyst such as $ZnCl_2$. The following preferred reactions have been successfully conducted:



The method of the instant invention is illustrated by the production of polyisobutylene functionalized with terminal azido, cyano, carbonylamino or thiocarbonylamino groups. In preferred embodiments of the invention, isobutene monomer is provided in a low-boiling, low-freezing alkyl halide solvent. An azido-
 5 providing species such as a substituted benzylic type azide such as cumyl azide may be added to the monomer. Functionalization by the azide, cyano, carbonylamino, cyanato, thiocyanato, isothiocyanato, or thiocarbonylamino group can be obtained during the cationic polymerization of the selected monomer (e.g., isobutylene) in the liquid phase. To achieve this result, the azide, cyano, carbonylamino, cyanato,
 10 thiocyanato, isothiocyanato, or thiocarbonylamino group is introduced in the form of a suitably designed molecule including a release moiety enabling the Y- group to migrate to the electrophilic site of a growing polymer chain.

It is believed that the polymerization in accordance with the process of the present invention is a living cationic polymerization. In such a system, the degree of
 15 polymerization is equal to the concentration of monomer consumed and incorporated in the polymer divided by the initiator concentration. If the rate of initiation is equal to or higher than that of propagation, living polymerizations will yield molecular weight distributions very close to unity; i.e., M_w/M_n is about equal to 1. This latter requirement is not disclosed to be part of the rigorous definition of living
 20 polymerization. Initiation and propagation can be separated and controlled individually, for example, by first preparing a quantity of active centers and subsequently adding monomer to this seed or by continuously adding monomer to the active centers. It is believed that in accordance with the present invention, N-
 25 containing initiators having Y- groups, which are mobile in the presence of Friedel-Crafts catalysts, provide functionalization (during polymerization) of the growing polymer chain ends. This is believed to occur by reaction of the electrophilic site with the complex anion containing the Y- constituent. The introduction of the initiator (also
 30 herein sometimes termed the "cocatalyst") simultaneously provides an initiation site and a functionalization system enabling the following reaction:



where R is the release moiety of the cocatalyst, N_3 is the nitrogen-containing functional group, Cat is, for instance, a metal halide catalyst, and m is the degree of
 35 polymerization.

In the case of monofunctional N-containing initiators of this invention (e.g., $\phi C(CH_3)_2N_3$), the resulting product then theoretically contains functionality at each end. That is, one end of the polymer corresponds to the R group of the nitrogen-

containing initiator and the other corresponds to the Y group of the initiator. In the case of a difunctional initiator of this invention e.g.,

$N_3C(CH_3)_2[phenylene]C(CH_3)_2N_3$, the resulting polymer product will theoretically contain a Y functionality at each end of the polymer, and a R group within the polymer chain. The RY_n initiator compound, when $n > 2$, is multifunctional and additional branching of the polymer can occur due to polymer growth at multiple sites on the initiators of this invention. In the living polymerization method of the present invention the polyolefin branches are ideally all of the same length. The branches emanate from the R group in a star-like structure. In the above reactions the Y-group (e.g., the -N₃, azide group) in the N-containing initiator has sufficient mobility to be transferred to the growing chain end. Preferably, the Lewis Acid selected to catalyze the polymerization is introduced at a concentration corresponding to greater than three times, preferably four and more, preferably from four to twenty times, the molar equivalents of the Y functional group, i.e., azide or other N-containing group of this invention, charged to the polymerization zone.

The preferred N-containing initiators employed in this invention are those in which the Y group is covalently bound to a secondary or tertiary carbon, and those in which the R release moiety is resonance stabilized or otherwise capable of delocalizing charge. Preferably the R release moiety is an allylic or benzylic species. The initiator can be monofunctional, di- or multifunctional, and can contain more than one of the above Y functional groups, although it is preferred that di- or multifunctional initiators contain only a single such type of Y group. The functionality of the polymer product is then equal to one, two or more, accordingly. Preferred initiator molecules include 1-azido-1-methylethyl benzene, and 2-azido-2-phenylpropane in which the azide group is at the same time tertiary and of the benzylic type, and bis(1-azido-1-methylethyl)benzene. Hydrazoic acid is also useful as the initiator molecule containing an azide group. In the latter case, the proton of the acid is the fragment on which polymerization is initiated (by cocatalysts), and the functionalization is the result of the termination reaction. Particularly preferred is bis(1-azido-1-methylethyl)benzene, and the compounds derived therefrom. In particular, where the two azide groups were replaced by any one of the members of the pseudohalide functions it was possible to obtain the synthesis of end-capped oligomers in an ideal situation, i.e., specific functionalization with nitrogen-containing groups, low polydispersity and predetermined molecular weight, without the help of any substance of the electron donor type (provided that the concentration of the Lewis acid is adjusted to a proper value which is higher than that of the nitrogen containing function).

The catalyst can comprise a Friedel-Crafts catalyst or other Lewis Acid cationic

polymerization catalyst. The Friedel-Crafts catalyst can comprise an organometallic compound of the formula $R^9_{n'}M'T_{n''}$ wherein M' is a metal selected from the group consisting of Ti, Al, Sn, Fe and Zn, R^9 is a hydrocarbyl group (preferably a C_1 to C_7 alkyl group, and most preferably a C_1 to C_4 alkyl group), T is a halogen or mixture of halogens, preferably chlorine or bromine, and most preferably chlorine, or a group of atoms corresponding to the conjugated base of strong Bronsted acids such as ClO_4^- or $CF_3SO_3^-$, and wherein n' is an integer of from 0 to $(v - 1)$ and n'' is an integer of from 1, wherein v is the valence of M' , with the proviso that $(n' + n'')$ is less than or equal to v . Preferred are organoaluminum halides, aluminum halides, boron trifluoride, and titanium halides. Most preferred are organoaluminum chlorides. The foregoing organometallic halide compounds are known in the art and can be prepared by conventional means, e.g., by the process described in U.S. Patent No. 4,151,113 and the references cited therein. Other Lewis Acid catalysts comprise metal halides (preferably chlorides or bromides), e.g., B and As, such as BCl_3 , BF_3 , AsF_5 , and the mixed halides thereof such as $BClF_2$, and the various "sesqui" derivatives of elements of Group IIIA (Group 13 in the new notation) of the Periodic Table of the Elements, such as $B_2(C_2H_5)_3(CF_3SO_3)_3$, $Al_2(C_2H_5)_3Cl_3$, and the like. Preferred catalysts are amongst the relatively "weak" Lewis acids such as diethylaluminum chloride, ethylaluminum dichloride. Stronger Lewis acids, such as boron trichloride or titanium tetrachloride, depending on the solvent and monomer used, are useful although not preferred since control of molecular weight and MWD is not as good as with the "weak" Lewis acids. When the Lewis acids are too weak, no polymerization is observed. Most preferred Friedel-Crafts Lewis acid catalysts are organoaluminum halides.

Although insoluble catalysts may be used, the catalyst is preferably soluble in the reaction medium, and the exact concentration of the catalyst depends on the concentration of the molecule containing the Y group. Preferably, the Lewis acid catalyst and N-containing initiator are charged to the polymerization zone in moles of Lewis Acid catalyst to moles of initiator in a ratio of greater than 3:1 to 1, preferably from 4:1 to 30:1, and more preferably from 5:1 to 20:1, a particularly useful range of greater than 6:1 and specifically greater than 6.1:1. Molecular weight of the product may be controlled by controlling the ratio of the moles of monomer M to moles of initiator I; molecular weight increases as this latter ratio increases.

Suitable solvents include, but are not limited to, low-boiling alkyl halides, whether they are mono- or polyhalides, the requirement being a reasonably low freezing point to be used at the preferred polymerization temperature. Illustrative diluents or solvents useful in cationic polymerization include alkanes (generally C_2 to C_{10} alkanes, including normal alkanes such as propane, n-butane, n-pentane, n-

hexane, n-heptane, and branched alkanes including isobutane, isopentane, isohexane, 3-methylpentane, and the like), alkenes and alkenyl halides (such as vinyl chloride), carbon disulfide, chloroform, ethylchloride, N-butyl chloride, methylene chloride, methylchloride, 1,2-dichloroethane, carbon tetrachloride, nitroethane, neopentane, benzene, toluene, and methylcyclohexane. Mixed solvents can also be used. The preferred solvents are methyl and ethyl chloride, methylene dichloride and propyl chloride, hexane, heptane and purified petroleum ether.

Any cationically polymerizable monomers may be used, including straight and branched chain alpha olefins, isoolefins, alicyclic monoolefins, cycloaliphatic compounds, styrene derivatives, indene and derivatives, and other monoolefins and heterocyclic cationically polymerizable monomers identified in the text by J.P. Kennedy "Cationic Polymerization of Olefins: A Critical Inventory" pages 39 to 53 (John Wiley & Sons, 1975). Vinyl ethers can also be used.

Particularly valuable polymers can be prepared from isoolefins of from 4 to 20 carbon atoms or mixtures thereof to produce homopolymers and copolymers. Examples of such unsaturated hydrocarbons include, but are not restricted to, isobutylene, 2-methylbutene, 3-methylbutene-1, 4-methylpentene-1, and beta-pinene. Other cationically polymerizable monomers which may be employed include heterocyclic monomers such as oxazolines and others known to add onto polarized covalent bonds. Mixtures of cationically polymerizable monomers can be employed as feedstock to the polymerization zone if desired, e.g., copolymers, terpolymers and higher interpolymers can be prepared by employing a mixture of two, three or more of the above monomers. Preferred feedstocks to the polymerization zone comprise pure isobutylene and mixed C₄ hydrocarbon feedstocks containing isobutylene, such as a C₄ cut resulting from the thermal or catalytic cracking operation of, for example, naphtha. Thus, suitable isobutylene feedstocks will typically contain at least 10%, and up to 100% isobutylene, by weight, based on the weight of the feed. In addition to isobutylene, conventional C₄ cuts suitable for use as a feedstock which are of industrial importance typically will contain between about 10 and 40% butene-1, between about 10 and 40% butene-2, between about 40 and 60% isobutane, between about 4 and 10% n-butane, and up to about 0.5 butadiene, all percentages being by weight based on the feed weight. Feedstocks containing isobutylene may also contain other non-C₄ polymerizable olefin monomers in minor amounts, e.g., typically less than about 25%, preferably less than about 10%, and most preferably less than 5%, such as propadiene, propylene and C₅ olefins. The term "polyisobutene" as employed herein is intended to include not only homopolymers of isobutylene but also copolymers of isobutylene and one or more other C₄ polymerizable monomers of conventional C₄ cuts as well as non-C₄ ethylenically

unsaturated olefin monomers containing typically from 3 to 6, and preferably from 3 to 5 carbon atoms, provided such copolymers contain typically at least 50%, preferably at least 65%, and most preferably at least 80% isobutylene units, by weight, based on the polymer number average molecular weight (Mn). The substantially selective
5 polymerizability of isobutylene under the conditions specified herein ensures the aforescribed minimum isobutylene content.

Preferably the polymerization medium is substantially free of substances which are capable of initiating the catalysts other than the selected N-containing initiator (or mixtures of initiators) of this invention. Therefore, the polymerization medium
10 preferably should be substantially free of added conventionally employed cationic polymerization initiators or promoters (i.e., cocatalysts) such as water, alcohols, carboxylic acids and acid anhydrides, HF, ethers or mixtures thereof. The alcohols which should be excluded are straight or branched chain, aliphatic, aromatic, or mixed aliphatic/aromatic alcohols containing from 1 to 30 carbon atoms. Likewise,
15 the carboxylic acid, acid anhydride and/or ether promoters to be excluded are halogen substituted or unsubstituted, straight or branched chain, aliphatic, aromatic or mixed aliphatic/aromatic acids and ether containing from 1 to 30 carbon atoms. The polymerization reaction medium preferably contains less than 20 weight ppm of water, and less than 5 weight ppm of mercaptans, all of which can function as poisons
20 to Lewis Acid catalysts. The olefin feed can be treated to achieve the above desired levels by conventional means, e.g., by use of mole sieves and caustic washing to remove mercaptans and water to the above, and dienes (if desired).

The polymerization reaction may be conducted batchwise or in semicontinuous or continuous operation in which continuous streams of ingredients are delivered to
25 the reactor, and an overflow of a slurry or solution of polymer is taken out for the recovery of the polymer therefrom. The preferred mode of reaction, however, is on a continuous basis using a continuous flow stirred reactor wherein feed is continuously introduced in a controlled manner into the reactor and product continuously removed in a controlled manner from the reactor.

30 The amount of Lewis Acid catalyst employed in the process of the present invention can be controlled in conjunction with the reaction temperature to achieve the target number average molecular weight of polymer but is also sought to be minimized to reduce undesired isomerizations believed to be induced thereby. The lower the initiator concentration in the reaction phase, the higher will be the polymer
35 molecular weight and vice versa. Control of the polymer molecular weight within defined limits of a selected target polymer molecular weight is particularly important when the polymer is intended for use in lubricating oils as a dispersant. The catalyst amount also affects the conversion of the olefin monomer and yield of polymer, with

higher amounts of Lewis Acid catalyst typically achieving higher conversions and yields. Strong Lewis Acid catalyst can lead to isomerizations which reduce the functionality of the polymer, and can produce chain transfer. Thus, in the process of the present invention, a weaker or milder Lewis acid is preferred. In view of the
5 above, and of the fact that the Lewis Acid is complexed more or less strongly by the nitrogen-containing groups present in the reaction medium, the catalyst should be employed in sufficient amount to enable the reaction to be a "living" cationic polymerization. In other words, the preferred catalyst concentration corresponds to about the quantitative formation of complex between the catalyst and the nitrogen-
10 containing compound. More specifically, the catalyst employed at a ratio of moles of Lewis Acid to equivalents of nitrogen-containing functional groups of more than 3.1:1, preferably more than 4:1, more preferably more than 6:1, with a preferred range of from 3.1:1 to 30:1, more preferably 4:1 to 20:1 and most preferably 6:1 to 10:1. When using bifunctional initiators, the Lewis acid to initiator molar ratios is preferably from
15 3:1 to 5:1.

The polymerization reaction is conducted in the liquid phase to induce linear or chain type polymerization in contradistinction to ring or branch formation. If a feed is used which is gaseous under ambient conditions, it is preferred to control the reaction pressure and/or dissolve the feed in an inert solvent or liquid diluent, in order to
20 maintain the feed in the liquid phase. Typical C₄ cuts comprising the feed are liquid under pressure and do not need a solvent or diluent. Where the selected Lewis Acid catalyst is normally a gas (e.g., BF₃, and the like) the catalyst is typically introduced into the reactor as gas which is partially or completely dissolved in a pressurized liquid in the reactor. Polymerization pressures can range typically from 25 to 500,
25 and preferably from 100 to 300, kpa.

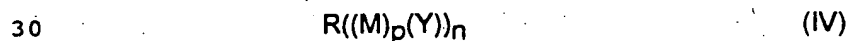
The N-containing initiator can be introduced to the monomer feed, or to the reaction mixture, in liquid form preferably separately from the Lewis Acid catalyst. Preferably, the monomer is not contacted with the Lewis Acid catalyst in the absence of the N-containing initiator of this invention.

30 The temperature at which the polymerizations are carried out is important, since temperatures which are too high tend to decrease the functionalization degree. The usual polymerization temperature range is between 100°C and +10°C. Preferably, the polymerizations are performed at a temperature below -10°C, preferably below -20°C, and preferably between -80°C and -20°C, e.g. at a
35 temperature of -50°C. The liquid phase reaction mixture temperature is controlled by conventional means. The particular reaction temperature is selected to achieve the target living polymerization behavior, and preferably is not allowed to vary more than + or -5°C from the selected value, while the catalyst and/or promoter feed rate is

Average polymerization times, in minutes, can vary from 10 to 120, preferably from 15 to 45 (e.g., 20 to 30), and most preferably from 15 to 25.

The materials used to quench the reaction are conventional and include the same materials conventionally used as cationic polymerization promoters (e.g., moisture, alcohol) with the exception that excess quantities are employed in amounts sufficient to deactivate the catalyst. Thus, while any amount of quenching medium effective to deactivate the catalyst may be employed, it is contemplated that such effective amount be sufficient to achieve a molar ratio of quench medium to Lewis Acid catalyst of typically from 1:1 to 100:1, preferably from 3:1 to 50:1, and most preferably from 10:1 to 30:1. Quench is conducted by introducing the quench medium into the polymer product. Typically, the polymer product is maintained under pressure during the quench sufficient to avoid vaporization of any gaseous Lewis Acid catalyst (if one is employed) and other components of the mixture. The temperature of the quenching medium is not critical and, e.g., can comprise room temperature or lower. In a batch system, quench can be performed in the reactor or preferably on the product after it is withdrawn from the reactor. In a continuous system, the quench will typically be performed after product exits the reactor. After quench, the polymerization product is typically subjected to conventional finishing steps which include a caustic/H₂O wash to extract catalyst residue, a hydrocarbon/aqueous phase separation step wherein deactivated and extracted Lewis Acid catalyst is isolated in the aqueous phase, and a water washing step to remove residual amounts of neutralized catalyst. The polymer is then typically stripped in a debutanizer to remove unreacted volatile monomers, followed by a further stripping procedure to remove light end polymer (e.g., C₂₄ carbon polymer). The stripped polymer is then typically dried by N₂.

The present invention includes a polymer composition having the formula:



R is selected from at least one group consisting of H, a hydrocarbyl group, and a hydrocarbyl-substituted silyl group. R can be alkyl, aryl, alkylaryl and arylalkyl. Y is selected from at least one group consisting of an azido, cyano, carbonylamino, thiocarbonylamino, cyanato and thiocyanato. A preferred Y is an azido group. M is at least one repeat unit derived from a cationically polymerizable monomer. Useful monomers include straight and branched chain alpha olefins, isoolefins, alicyclic monoolefins, cycloaliphatic compounds, styrene derivatives, indene and derivatives

thereof, and other monoolefins and heterocyclic monomers. p is an integer greater than 1 and preferably sufficient to attain a desired molecular weight. n is an integer of at least 1, preferably 1 to 10 and most preferably 1 to 2.

The novel polymers of this invention comprise terminally substituted polymers
5 derived from any of the above-discussed cationically polymerizable monomers. The polymers will preferably contain at least 5 monomer units (M) per polymer chain, and will more usually be characterized by number average molecular weights of at least 350 or less and up to 15,000,000 or more with a useful range of from 350 to 15,000,000. The molecular weight range can be determined for particular polymers.
10 However, preferred polymers generally range from 500 to 2,000,000 with derivatives of functionalized polymer used as lubricant additives generally up to 100,000 and with specific ranges of from 500 to 20,000 for use as dispersants and 20,000 to 100,000 for use as viscosity improvers. The polymerization of the present invention can be conducted in a manner and under conditions to attain various molecular weight
15 polymers. Low molecular weight polymers are considered to be polymers having a number average molecular weight of less than 20,000, preferably from 500 to 10,000, (e.g. from 2,000 to 8,000) and most preferably from 1,500 to 5,000. Molecular weights in this range are conveniently measured by vapor phase osmometry. Low molecular weight polymers are useful in forming dispersants for lubricant additives.
20 Medium molecular weight materials having a number average molecular weight range of from 20,000 to 200,000, preferably 25,000 to 100,000; and more preferably from 25,000 to 80,000 are useful for viscosity improvers for lubricating oil compositions, adhesive coatings, tackifiers and sealants. The medium number average molecular weights can be determined by membrane osmometry. The higher molecular weight
25 materials have a number average molecular weight range of greater than 200,000 to 15,000,000, specifically 300,000 to 10,000,000 and more specifically 500,000 to 2,000,000. These polymers are useful in polymeric compositions and blends including elastomeric compositions. Higher molecular weight materials having number average molecular weights of from 20,000 to 15,000,000 can be measured by
30 gel permeation chromatography with universal calibration, or by light scattering. The values of the ratio M_w/M_n , also referred to as molecular weight distribution, (MWD) are not critical. However, a typical maximum M_w/M_n value of 1.5 is preferred with typical ranges of 1.1 up to 1.4. The ideal MWD is 1.0.

Useful olefin monomers from which nitrogen-containing polyalkenes of the
35 present invention can be derived are polymerizable monoolefin monomers characterized by the presence of one or more groups having carbon-carbon unsaturated double bonds (i.e., $>C=C<$); that is, they are monoolefinic monomers such as ethylene, propylene, butene-1, isobutene, and octene-1 or polyolefinic

monomers (usually diolefinic monomers) such as butadiene-1,3 and isoprene. Although the polyalkenes may include aromatic groups (especially phenyl groups and lower alkyl- and/or lower alkoxy-substituted phenyl groups such as para-(tert-butyl)phenyl and cycloaliphatic groups such as would be obtained from polymerizable

5 cyclic olefins or cycloaliphatic substituted-polymerizable acrylic olefins, the polyalkenes usually will be free from such groups. Again, because aromatic and cycloaliphatic groups can be present, the olefin monomers from which the polyalkenes are prepared can contain aromatic and cycloaliphatic groups. Specific

10 examples of polyalkenes include polypropylenes, polybutenes, ethylene-propylene copolymers, ethylene-tert-butene, styrene-isobutene copolymers, isobutene-(paramethyl)styrene copolymers, copolymers of octene-1, copolymers of 3,3-dimethyl-pentene-1 with hexene-1, and copolymers of isobutene and styrene. Also included are the poly(isobutene)s obtained by polymerization of C₄ refinery stream

15 having a butene content of about 35 to about 75% by weight and an isobutene content of about 30 to about 60% by weight. These polybutenes contain predominantly (greater than about 80% of the total repeating units) of isobutene repeating units of the configuration:



25 Also useful are poly-n-butenes made by the process of the present invention. A preferred source of n-butenes is petroleum feedstreams such as Raffinate II. These feedstocks are disclosed in the art such as in U.S. Patent No. 4,952,739. These C₄ feedstreams preferably is substantially free of sulfur contaminants (e.g., mercaptans) e.g. <20 wppm H₂S and 5 wppm S and is preferably substantially

30 anhydrous, that is, it contains less than 300 wppm water, based on the C₄ monomers in the feedstream as well as less than 100 ppm of methanol (which may be present if the feedstream is derived from Raffinate I used to make MTBE). The C₄ products other than butenes (e.g., saturated C₄ hydrocarbons), functions as diluent or solvent in the reaction mixture and are a non-critical aspect of this invention. The process of

35 the present invention has enabled a new class of polymers and copolymers to be made from Raffinate II feedstock rendering a substantially low value feedstream as a valuable new raw material.

The living polymers of the present invention will comprise terminal substituent Y groups on one end, and a terminal R group on the other end when the nitrogen-

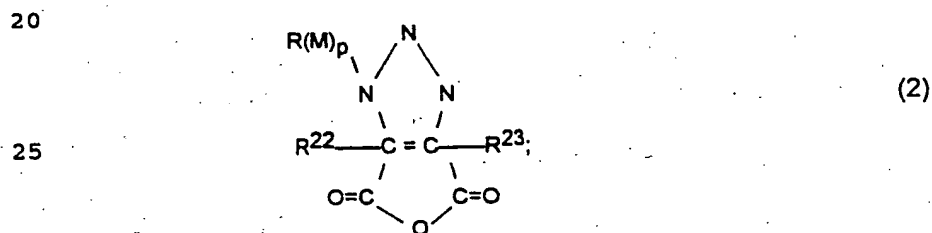
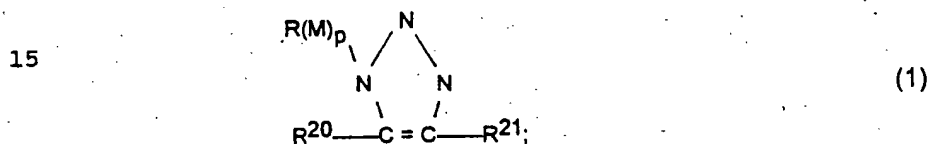
containing initiator comprises a R-Y or R*-Y compound. R and R* are discussed above with regard to formulae (Ia, Ib and Ic). The resulting polymers have the following structures: R-[polyolefin]-Y; and R*-[polyolefin]-Y. When a poly-functional initiator is employed, such as the bifunctional initiator of Formula III above, the
5 polymers will comprise terminal Y-groups on each end of the polymer and a R group within the polymer chain, e.g., substantially at the center of the polymer chain. The poly-substituted polymers of this invention have the following structure: Y-[polyolefin]-R-[polyolefin]-Y.

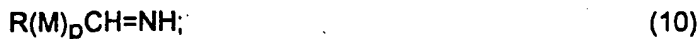
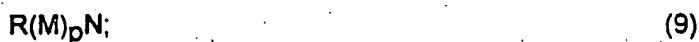
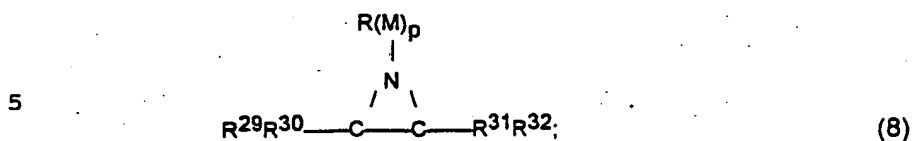
The nitrogen functionalized polymeric materials of the present invention are
10 useful by incorporation and dissolution into an oleaginous material such as fuels and lubricating oils. When the polymers of this invention are used in normally liquid petroleum fuels such as middle distillates boiling from about 65°C to 430°C, including kerosene, diesel fuels, home heating fuel oil, jet fuels, etc., a concentration of the polymers in the fuel will be in the range of typically from 0.001 to 0.5, and preferably
15 0.005 to 0.15 wt. %, based on the total weight of the composition. When the polymers of this invention are used in lubricating oils, a concentration of the polymers in the lubricating oil is in the range of from 0.01 to 15 wt. %, and preferably 0.5 to 10 wt. %, based on the total weight of the lubricating composition. The polymers may be employed in lubricating oil compositions which employ a base oil in which the
20 polymers are dissolved or dispersed. Such base oils may be natural or synthetic. Base oils suitable for use in preparing the lubricating oil compositions of the present invention include those conventionally employed as crankcase lubricating oils for spark-ignited and compression-ignited internal combustion engines, such as automobile and truck engines, marine and railroad diesel engines, and the like.
25 Advantageous results are also achieved by employing the polymers of the present invention in base oils conventionally employed in and/or adapted for use as power transmitting fluids such as automatic transmission fluids, tractor fluids, universal tractor fluids and hydraulic fluids, heavy duty hydraulic fluids, power steering fluids and the like. Gear lubricants, industrial oils, pump oils and other lubricating oil
30 compositions can also benefit from the incorporation therein of the polymers of the present invention. These lubricating oil formulations conventionally contain several different types of additives that will supply the characteristics that are required in the formulations. Among these types of additives are included viscosity index improvers, antioxidants, corrosion inhibitors, detergents, dispersants, pour point depressants,
35 antiwear agents, friction modifiers, etc.

The polymers of this invention are also useful as polymerization additives, e.g. as cross-linking agents and polymerization comonomers, and the polymers can be employed to prepare molded or extruded articles such as films. The polymers of this

invention are also useful components for the synthesis of block copolymers and star copolymers. These polymer materials can be used as compatibilizer or as thermoplastic elastomers.

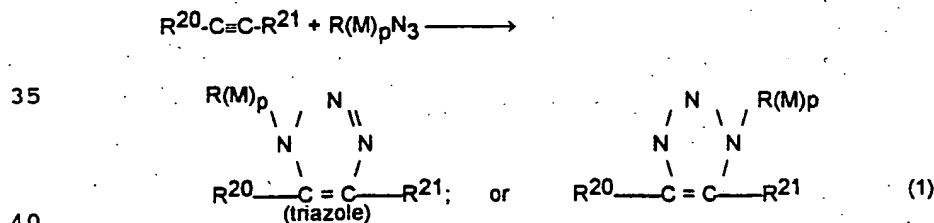
The polymers of the present invention include functional reaction products of the above-recited polymers containing nitrogen groups, particularly -N₃, -NCO, -OCN, -SCN, -CN and -NCS groups. Such functional reaction products are the reaction product of the nitrogen functional groups of the nitrogen-containing polymer with a functional reactant compound. This is illustrated by the reaction of -N₃ (azido) containing polymer derived from formula IV, where -Y is -N₃, i.e., (R(M)_p(-N₃))_n where R, M, p and n are as defined above. For illustration purposes n equals one. The azido R(M)_p-N₃ can be reacted to form functional reaction product polymers containing the following functional groups:



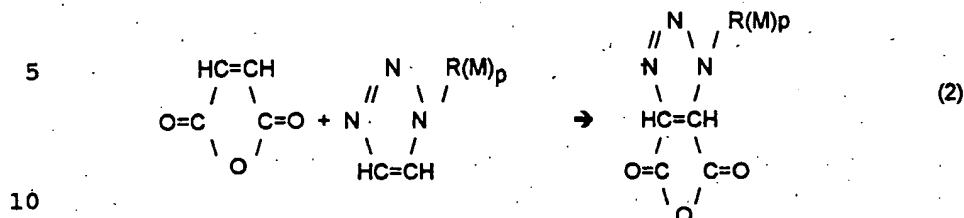


wherein R^{20} to R^{33} are the same or different and can be selected from hydrogen, a hydrocarbonyl group and a substituted hydrocarbonyl group. R^{20} to R^{33} can be -H, and
 20 alkyl, aryl, alkylaryl, or arylalkyl group, X is a halide, preferably a chloride group. Useful R^{20} to R^{33} alkyl groups include C_1 to C_{22} hydrocarbonyl groups with methyl, ethyl, propyl and butyl groups being particularly useful. Reactions of azides to
 25 prepare the above functional reactant product polymers include those of types known in the art. Typically, they can be conducted under mild conditions in a suitable solvent. A useful solvent is tetrahydrofuran (THF) at 0°C - 100°C and 1 atmosphere. The above functional reactant azide polymeric compounds can be prepared according to methods analogous to those disclosed.

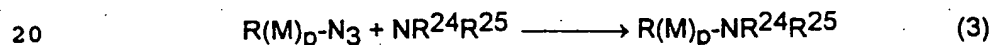
Bastide et al., Cycloaddition dipolaire-1,3 aux alcynes, Bulletin De La Societe Chimique De France Nos. 7-8, pp. 2555 - 2579 (1973), discloses a variety of
 30 reactions of azides beginning at p. 2574. A useful reaction of the present invention to form a polymer triazoles useful as lubricant additives is:



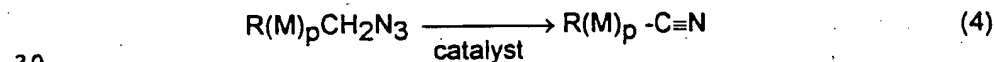
Bastide et al., Cycloaddition dipolaire-1,3 aux alcynes, Bulletin De La Societe Chimique De France, Nos. 9-10, pp. 2871 - 2887 (1973), discloses a variety of reactions including the reactions of triazoles. A useful reaction of the present invention is the reaction of an anhydride, preferably maleic anhydride with a triazole.



Compounds of formula (2) are useful as additives in lubricant compositions and they can be further reacted with alcohols, metals, metal compounds and amines to form polymeric compounds which are also useful as lubricant additives. Kazankov et al., J. Org. Chem. USSR 77,451 (1975) discloses the replacement of azo compounds; the reaction can be applied to the azide functionalized polymer of the present invention:

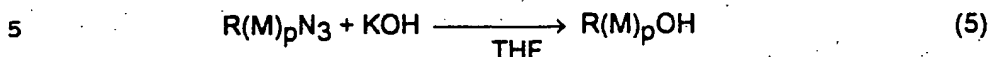


Preferably at least one of R²⁴ and R²⁵ is an -H group. With a preferred embodiment of formula (3) being R(M)_pNH₂; this amine can be used as an additive for lubricants. The conversion of azides to nitriles is disclosed in the Bull. Chem. Soc. of Japan, 49 p. 506 (1976) and the J. Org. Chem., Vol. 44, No. 16, p. 2951 (1976); applied to decomposition of an azide of the present invention:

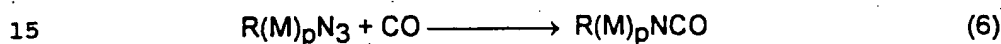


the R(M)_pC≡N can be further reacted to form an amine, i.e., with H₂ to form R(M)_pCNH₂. The catalyst can be Pd or those referred to in the above publications. The amine is useful as an additive for lubricating oils. An alternative and preferred method of producing amine derivatized polymer from azido functionalized polymer is by reducing the azido group to form an amine group. The reduction is preferably accomplished by reducing the azido functionalized polymer in the presence of a reducing catalyst to form the amine. Useful reducing catalysts include LiAlH₄, CaH₂ and the like, with LiAlH₄ most preferred. The reaction is preferably conducted in a suitable solvent for the polymer and the catalyst, preferably a polar solvent such as tetrahydrofuran (THF). The reaction can be conducted at room temperature or under reflux conditions.

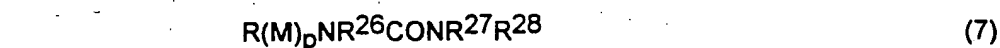
Knudsen et al., A Convenient One-Step Conversion of Aromatic Nitro Compounds to Phenols, J. Org. Chem., Vol. 39, No. 23, 1974, discloses conversion of phenolic azido to esters; as applied herein:



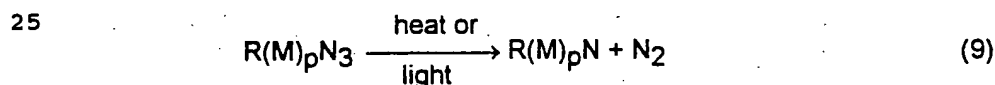
Other hydroxyl type bases and solvents for the base and polymer can be used, with KOH preferred. The polymer containing hydroxyl group can be reacted with acids, i.e. carboxylic acids to form esters which are useful as additives for lubricating oil compositions. Isocyanates can be formed by the reaction of azides and CO as disclosed in J. Am. Chem. soc. 90, 3295 (1968); the reaction can be applied herein as follows:



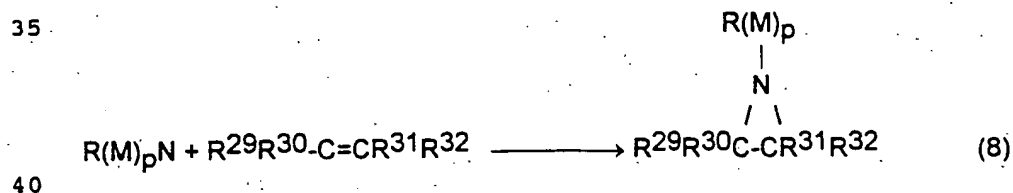
The $R(M)_pNCO$ can be reacted with an amine to form



which is useful as a lubricant additive. Preferably R^{26} is -H, and at least one of R^{27} and R^{28} is -H. Nitrogens can be formed from azides by decomposing by heat or light.

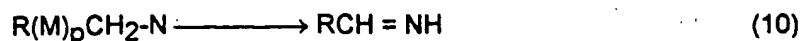


The J. Am. Soc. Chem. Comm., 1160 (1922) and Anderson et al., Addition of Nitrenes to Acetylene. Anti-aromaticity of 1-H-Azirines, Chemical Communications, 147 (1969) discloses chemistry related to the addition of nitrenes to acetylenes. The nitrene reacts with a compound having a carbon-carbon double bond as follows:



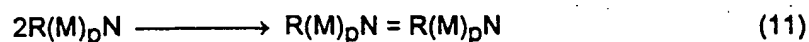
The nitrenes of formula (9) can rearrange to form imines. This type of chemistry is reviewed in Moriarty et al., The Direct and Photosensitized Decomposition of Alkyl Azides, Tetrahedron, 26, 1379 (1970) and J. Am. Chem. Soc. 93, 1537 (1971):

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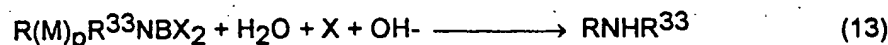
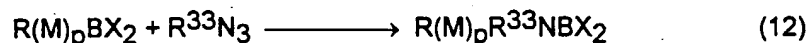
Dimerization reactions of nitrenes are reviewed in Smith, in Lwowski; Nitrenes, Ref. 200, p. 112, pp. 405 - 419, and usefully applied as follows:

10



The J. Am. Chem. Soc. 94, p. 2114 (1973) and 95, 2394 (1973) disclose the reaction of azides with chloroboranes to form secondary amines:

15



20



The functionalized reactant product polymer can be used as a dispersant if the functional group contains the requisite polar group. However, derivatives of various of the functionalized polymers can be formed. These derivatized polymers have the requisite properties for uses such as dispersants and viscosity modifiers.

Reactant functional groups of the functionalized polymer can be reacted with derivative compounds to form derivatized polymers. The derivative compound comprises at least one reactive derivative group. The derivatized compound preferably contains at least one additional group which makes the derivatized group polar or reactive. Such derivatized polymers can contain amine groups, carboxyl groups or groups derived from reactive metal or reactive metal compounds. Various of the functional reactant product polymers can be further chemically modified to improve the polymer properties or impart desirable properties not otherwise present. A chemical moiety can be directly or indirectly reacted at various of the nitrogen-containing functional reactant groups included in formulae (1) to (14). Such modified, derivatized compounds include the reaction product of formula (2), particularly

wherein the anhydride is maleic anhydride, with derivative compounds, and formula (6), isocyanato, with compounds containing carboxyl groups. The functionalized polymer having the amine groups of formulae (3) and (14), and alcohol groups of formula (5) can be used directly, i.e. as dispersants or V.I. improvers for lubricating oil compositions or further derivatized with carboxyl-containing derivative compounds. The derivatized polymer can include the reaction product of the above recited functionalized polymer (i.e. formula (2)) with a nucleophilic reactant such as amines, alcohols, amino-alcohols and mixtures thereof to form oil soluble salts, amides, imides, oxazoline and esters of mono- and dicarboxylic acids, esters or anhydrides. The derivatized polymers are useful as lubricant dispersants which maintain oil insolubles (resulting from oxidation during use) in suspension in the fluid, thus preventing sludge flocculation and precipitation. The compounds useful as dispersants generally are characterized by a polar group attached to a relatively high molecular weight hydrocarbon chain. The polar group generally contains up to 10 wt. %, and typically from 0.1 to 5 wt. %, of one or more of the elements nitrogen, oxygen, sulfur and phosphorus. The solubilizing chains are generally higher in molecular weight than those employed with the metallic based dispersants, but in some instances they may be quite similar. Various types of dispersants can be made using the derivatized polymer of the present invention and are suitable for use in the lubricant compositions. The following are illustrative:

1. Reaction products of carboxylic acid or anhydride functionalized reactant polymer, i.e. formula (2) of the present invention (or derivatives thereof) derivatized with nitrogen-containing compounds such as amine, organic hydroxy compounds such as phenols and alcohols, and/or basic inorganic materials.
2. Reaction products of the acid or anhydride derivatized polymer (formula (2)) of the present invention which have been halogenated.
3. Reaction products, or isocyanato derivatized polymer (formula (6)) to form urea, and alcohols to form urethanes. Such reactions are typically conducted by mixing the component with or without solvents (depending on molecular weight) at ambient conditions. Reference is made to Morton, Rubber Technology 2nd Ed., Chapter 17, pp. 440. Van Nostrand Reinhold Co. (1973).

The derivatized living polymer can also be used to make ash and ashless type detergents. Typically, the living polymer for use as a detergent is an alkyl polymer having a number average molecular weight of from 300 to 900. The ash-producing

detergents are exemplified by oil-soluble neutral and basic salts of alkali or alkaline earth metals with alkyl derivatized polymer sulfonic acids, carboxylic acids, or organic phosphorus acids characterized by at least one direct carbon-to-phosphorus linkage such as those prepared by the derivatized olefin polymer of the present invention with

5 a phosphorizing agent such as phosphorus trichloride, phosphorus heptasulfide, phosphorus pentasulfide, phosphorus trichloride and sulfur, white phosphorus and a sulfur halide, or phosphorothioic chloride. The most commonly used salts of such acids are those of sodium, potassium, lithium, calcium, magnesium, strontium and barium. The term basic salt is used to designate metal salts wherein the metal is

10 present in stoichiometrically larger amounts than the derivatized polymer, such as with maleic anhydride (or acid) and methods for preparing such salts are well known in the art. Preferred ash-producing detergents which can be derived from the functionalized reactant polymer of the present invention include the metal salts of sulfonic acid derivatives, preferably wherein the polymer is an alkyl compound, alkyl

15 phenols, sulfurized alkyl phenols, alkyl salicylates, alkyl naphthenates and other oil soluble mono- and dicarboxylic acids. Highly basic (viz, overbased) metal salts, such as highly basic alkaline earth metal alkyl sulfonates (especially Ca and Mg salts) are frequently used as detergents and their production is well known in the art.

Useful amine compounds for derivatizing polymers having functional groups or

20 reactive derivative groups comprise at least one amine and can comprise one or more additional amines or other reactive or polar groups. Where the reactant functional group is a carboxylic acid, ester or derivative thereof, or an isocyanato, it reacts with the amine to form an amide. Where the functional group is a halide the amine reacts to displace the halide. Where the reaction functional group is an

25 isocyanate it reacts with an amine to form a urea, and an alcohol to form a urethane. Amine compounds useful as nucleophilic reactants for reaction with the functionalized polymer of the present invention include those disclosed in U.S. Patent Nos. 3,445,441, 5,017,299 and 5,102,566. Preferred amine compounds include mono- and (preferably) polyamines, of 2 to 60, preferably 2 to 40 (e.g. 3 to 20), total carbon

30 atoms of 1 to 12, preferably 3 to 12, and most preferably 3 to 9 nitrogen atoms in the molecule. These amines may be hydrocarbyl amines or may be hydrocarbyl amines including other groups, e.g., hydroxy groups, alkoxy groups, amide groups, nitriles, imidazoline groups, and the like. Hydroxy amines with 1 to 6 hydroxy groups, preferably 1 to 3 hydroxy groups, are particularly useful. Other useful amine

35 compounds include: alicyclic diamines such as 1,4-di(aminomethyl) cyclohexane, and heterocyclic nitrogen compounds such as imidazolines, and N-aminoalkyl piperazines. Commercial mixtures of amine compounds may advantageously be used. Low cost poly(ethyleneamine) compounds averaging 5 to 7 nitrogen atoms per

molecule are available commercially under trade names such as "Polyamine H", "Polyamine 400", "Dow Polyamine E-100", etc. Useful amines also include polyoxyalkylene polyamines. The polyoxyalkylene polyamines are commercially available and may be obtained, for example, from the Jefferson Chemical Company, Inc. under the trade name "Jeffamines D-230, D-400, D-1000, D-2000, T-403, etc. A particularly useful class of amines are the polyamido and related amines disclosed in U.S. Patent Nos. 4,857,217; 4,963,275 and 4,956,107. Preferred compounds for reaction with the polyamines in accordance with this invention are lower alkyl esters of acrylic and (lower alkyl) substituted acrylic acid.

The amine compound can be reacted with the functionalized polymer by heating an oil solution containing 5 to 95 wt. % of functionalized polymer to 100°C to 200°C, preferably 125°C to 175°C, generally for 1 to 10, e.g. 2 to 6 hours until the desired amount of water is removed. The heating is preferably carried out to favor formation of imides or mixtures of imides and amides, rather than amides and salts. Reaction ratios of dicarboxylic acid material to equivalents of amine as well as the other nucleophilic reactants described herein can vary considerably, depending upon the reactants and type of bonds formed. Generally from 0.1 to 1.0, preferably 0.2 to 0.6, e.g. 0.4 to 0.6, moles of functionalized groups present in the functionalized polymer is used, per equivalent of nucleophilic reactant, e.g. amine. For example, for imide formation, 0.8 mole of a pentamine (having two primary amino groups and 5 equivalents of nitrogen per molecule) is preferably used to convert polymer functionalized with succinic anhydride into a mixture of amides and imides, i.e. preferably the pentamine is used in an amount sufficient to provide 0.8 mole (that is $(2) (1.6)/[0.8 \times 5]$ mole) of carboxy functional groups (0.4 moles of succinic groups) per nitrogen equivalent of the amine. Tris(hydroxymethyl) amino methane (THAM) can be reacted with the aforesaid functionalized polymers to form amides, imides or ester type additives as taught by U.K. 984,409, or to form oxazoline compounds and borated oxazoline compounds as described, for example, in U.S. Patent Nos. 4,102,798; 4,116,876 and 4,113,639.

The polymers of the present invention functionalized with acid groups, i.e. formula (2), can be reacted with alcohols to form esters. The alcohols may be aliphatic compounds such as monohydric and polyhydric alcohols or aromatic compounds such as phenols and naphthols. The polymer containing isocyanato functionality reacted with alcohols to form urethanes. Phenol and alkylated phenols having up to three alkyl substituents are preferred. The alcohols from which the esters may be derived preferably contain up to 40 aliphatic carbon atoms. The polyhydric alcohols preferably contain from 2 to 10 hydroxy radicals. A useful class of polyhydric alcohols are those having at least three hydroxy radicals, some of

which have been esterified with a monocarboxylic acid having from 8 to 30 carbon atoms. The esters and urethanes may also be derived from unsaturated alcohols. Still another class of the alcohols capable of yielding the esters of this invention comprise the ether-alcohols and amino-alcohols. For the most part, the ether-

5 alcohols having up to 150 oxyalkylene radicals in which the alkylene radical contains from 1 to 8 carbon atoms are preferred. The esters may be diesters or acidic esters as well as mixtures. The esters may be prepared by methods known in the art. The method which is preferred because of convenience and superior properties of the esters it produces, involves the reaction of a suitable alcohol or phenol with the acid

10 or anhydride (i.e., functionalized polymer succinic anhydride). The esterification is usually carried out at a temperature above 100°C, preferably between 150°C and 300°C. The water formed as a by-product is removed by distillation as the esterification proceeds. A solvent may be used in the esterification to facilitate mixing, temperature control, and removal of water from the reaction mixture. Useful

15 solvents include xylene, toluene, diphenyl ether, chlorobenzene, and mineral oil. Esters obtained by the reaction of stoichiometric amounts of the acid reactant and hydroxy reactant are preferred. In some instances, it is advantageous to carry out the esterification in the presence of an acid catalyst or any other known esterification catalyst. Ester derivatives likewise may be obtained by the reaction of acid or

20 anhydride functionalized polymer with epoxide or a mixture of an epoxide and water. In lieu of the acid functionalized polymer, a polymer functionalized with lactone acid or a acid halide may be used in the processes above for preparing the ester derivatives of this invention. Such acid halides may be acid dibromides, acid dichlorides, acid monochlorides, and acid monobromides.

25 Where the carboxylic derivative compositions produced are esters, such esters include acidic esters and neutral esters. Acidic esters are those in which less than all of the functional groups in the functionalized polymer are esterified, and hence possess at least one free functional group. The functionalized, e.g. acid functionalized, polymers of this invention are reacted with the alcohols according to

30 conventional esterification techniques. This normally involves heating the functionalized polymer with the alcohol, optionally in the presence of a normally liquid, substantially inert, organic liquid solvent/diluent and/or in the presence of esterification catalyst. Temperatures of at least 100°C up to the decomposition point are used. This temperature is usually within the range of 100°C up to 300°C with

35 temperatures of 140°C to 250°C often being employed. Many issued patents disclose procedures for reacting high molecular weight carboxylic acids with alcohols to produce acidic esters and neutral esters. These same techniques are applicable to preparing esters from the functionalized polymer of this invention and the alcohols

described above. All that is required is that the acylating reagents of this invention are substituted for the high molecular weight carboxylic acid acylating agents discussed in these patents, usually on an equivalent weight basis.

Derivatized polymers can be prepared from reactive metal/metal compounds.

- 5 Useful reactive metals or reactive metal compounds are those which will form metal salts or metal-containing complexes with the functionalized polymer. Metal complexes are typically achieved by reacting the carboxyl functionalized polymers with amines and/or alcohols as discussed above, and also with complex forming reactants either during or subsequent to amination. Reactive metal compounds for
10 use in the formation of complexes with the reaction products of functionalized polymer and amines include those disclosed in U.S. Patent No. 3,306,908, Re. 26,433, U.S. Patent No. 3,271,310 and Canadian Patent No. 956,397. The processes of the references are applicable to the carboxylic derivative compositions of the functionalized polymer of this invention with the amines as described above by
15 substituting, or on an equivalent basis, the functionalized polymer of this invention with the high molecular weight carboxylic acid functionalized polymer disclosed in the patents. From the foregoing description, it is apparent that the appropriate functionalized reactive polymer of this invention can be reacted with any individual amine, alcohol, reactive metal, reactive metal compound or any combination of two or
20 more of any of these.

- Another aspect of this invention involves the post treatment of derivatized polymers. The processes for post-treating the functionalized or derivatized polymers useful as dispersant materials are analogous to the post-treating processes used with respect to conventional dispersants and multi-functional viscosity index improvers
25 useful as dispersants of the prior art. Accordingly, the same reaction conditions, ratio of reactants and the like can be used. Reference is made to U.S. Patent No. 5,017,199. Derivatized polymers can be post-treated with such reagents as urea, thiourea, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, nitriles, epoxides, boron compounds, phosphorus
30 compounds or the like. For example, the amine derivatized polymers can be treated with a boron compound selected from the class consisting of boron oxide, boron halides, boron acids and esters of boron acids in an amount to provide from 0.1 atomic proportion of boron for each mole of said nitrogen composition to 20 atomic proportions of boron for each atomic proportion of nitrogen of said nitrogen
35 composition. Borated derivatized polymers useful as dispersants can contain from 0.05 to 2.0 wt. %, e.g. 0.05 to 0.7 wt. % boron based on the total weight of said borated nitrogen-containing dispersant compound. Treating is readily carried out by adding from 0.05 to 4, e.g. 1 to 3 wt. % (based on the weight of said nitrogen

compound) of said boron compound, preferably boric acid which is most usually added as a slurry to said nitrogen compound and heating with stirring at from 135°C to 190°C, e.g. 140°C to 170°C, for from 1 to 5 hours followed by nitrogen stripping at said temperature ranges.

5 The derivatized polymers of the present invention can also be treated with polymerizable lactones (such as epsilon-caprolactone) to form dispersant adducts having the moiety $-\{C(O)(C_2)_zO\}_mH$, wherein z is a number of from 4 to 8 (e.g., 5 to 7) and m has an average value of from 0 to 100 (e.g., 0.2 to 20). The functionalized or derivatized polymers of this invention, particularly for use as a dispersant, can be
10 post-treated with a C_5 to C_9 lactone, e.g., epsilon-caprolactone, by heating a mixture of the polymers and lactone in a reaction vessel in the absence of a solvent at a temperature of 50°C to 200°C, more preferably from 75°C to 180°C, and most preferably from 90°C to 160°C, for a sufficient period of time to effect reaction. Optionally, a solvent for the lactone, dispersant material and/or the resulting adduct
15 may be employed to control viscosity and/or the reaction rates. Catalysts useful in the promotion of the lactone-dispersant material reactions are selected from the group consisting of stannous octanoate, stannous hexanoate, tetrabutyl titanate, a variety of organic-based acid catalysts and amine catalysts, as described on page 266, and forward, in a book chapter authored by R. D. Lundberg and E. F. Cox,
20 entitled "Kinetics and Mechanisms of Polymerization: Ring Opening Polymerization", edited by Frisch and Reegen, published by Marcel Dekker in 1969, wherein stannous octanoate is an especially preferred catalyst.

The above discussions relate to a variety of materials including the polymer per se, the functionalized polymer, the derivatized polymer, and post-treated
25 derivatized polymer. The polymer per se has a variety of utilities depending on its molecular weight including synthetic base oil (for lower molecular weights), adhesive coatings (for intermediate molecular weights), and as elastomeric compositions (for high molecular weights), e.g. films, extrudates, composites, and the like. The functionalized polymer, in addition to acting as intermediates for dispersant and in
30 multifunctional viscosity improvers (MFVI) manufacture, can be used as molding release agents, molding agents, metal working lubricants, paint thickeners, and the like. The primary utility for all the above described materials, from polymer all the way through post-treated derivatized polymer is as an additive for oleaginous compositions. For ease of discussion the above-mentioned materials are collectively
35 and individually referred to herein as "additives" when use in the context of an oleaginous composition containing such "additives". Accordingly, the additives of the present invention can be used by incorporation and dissolution into an oleaginous material such as fuels and lubricating oils. When the additives of this invention are

used in normally liquid petroleum fuels such as middle distillates boiling from 65°C to 430°C, including kerosene, diesel fuels, home heating fuel oil, jet fuels, etc., a concentration of the additives in the fuel in the range of typically from 0.001 to 0.5, and preferably 0.005 to 0.15 wt. %, based on the total weight of the composition, will usually be employed. Useful compositions and additives are disclosed in U.S. Patent No. 5,102,566.

The additives of the present invention find their primary utility in lubricating oil compositions which employ a base oil in which the additives are dissolved or dispersed therein. Such base oils may be natural or synthetic. Base oils suitable for use in preparing the lubricating oil compositions of the present invention include those conventionally employed as crankcase lubricating oils for spark-ignited and compression-ignited internal combustion engines, such as automobile and truck engines, marine and railroad diesel engines, and the like. Advantageous results are also achieved by employing the additive mixtures of the present invention in base oils conventionally employed in and/or adapted for use as power transmitting fluids, universal tractor fluids and hydraulic fluids, heavy duty hydraulic fluids, power steering fluids and the like. Gear lubricants, industrial oils, pump oils and other lubricating oil compositions can also benefit from the incorporation therein of the additives of the present invention. These lubricating oil formulations conventionally contain several different types of additives that will supply the characteristics that are required in the formulations. Among these types of additives are included viscosity index improvers, antioxidants, corrosion inhibitors, detergents, dispersants, pour point depressants, antiwear agents, friction modifiers, etc. The additives of this invention can be blended with a suitable oil-soluble solvent and base oil to form a concentrate, and then the concentrate is blended with a lubricating oil basestock to obtain the final formulation. Such dispersant concentrates will typically contain (on an active ingredient (A.I.) basis) from 10 to 80 wt. %, typically 20 to 60 wt. %, and preferably from 40 to 50 wt. % additive, and typically from 40 to 80 wt. %, preferably from 40 to 60 wt. % base oil, i.e., hydrocarbon oil based on the concentrate weight. The lubricating oil basestock for the additive typically is adapted to perform a selected function by the incorporation of additional additives therein to form lubricating oil compositions (i.e., formulations). Usually these concentrates may be diluted with 3 to 100, e.g., 5 to 40 parts by weight of lubricating oil, per part by weight of the additive package, in forming finished lubricants, e.g. crankcase motor oils. The purpose of concentrates, of course, is to make the handling of the various materials less difficult and awkward as well as to facilitate solution or dispersion in the final blend. Thus, the additive of the present invention and formulations containing them would usually be employed in the form of a 40 to 50 wt. % concentrate, for example, in a lubricating

oil fraction. The additives of the present invention will be generally used in admixture with a lube oil basestock, comprising an oil of lubricating viscosity, including natural and synthetic lubricating oils and mixtures thereof. Useful oils are described in U.S. Patent Nos. 5,017,299 and 5,084,197.

- 5 As indicated above, the additives of the present invention may be mixed with other types of additives selected to perform at least one desired function. Typical of such functions are detergent/inhibitor, viscosity modification, wear inhibitor, oxidation inhibitor, corrosion inhibitor, friction modifier, foam inhibitor, rust inhibitor, demulsifier, lube oil flow improvers, and seal swell control. As is well known in the art, some of
- 10 the additives can provide multiple effects e.g., a dispersant oxidation inhibitor. Compositions, when containing these additives, typically are blended into the base oil in amounts which are effective to provide their normal attendant function. Representative effective amounts of such additives are illustrated as follows:

15	<u>Compositions</u>	<u>Range</u>	
		<u>Broad</u>	<u>Preferred</u>
		<u>Wt %</u>	<u>Wt %</u>
20	Viscosity Index Improver	1-12	1-4
	Corrosion Inhibitor	0.01-3	0.01-1.5
	Oxidation Inhibitor	0.01-5	0.01-1.5
	Dispersant	0.1-10	0.1-5
	Lube Oil Flow Improver	0.01-2	0.01-1.5
25	Detergents and Rust Inhibitors	0.01-6	0.01-3
	Pour Point Depressant	0.01-1.5	0.01-1.5
	Anti-Foaming Agents	0.001-0.1	0.001-0.01
	Antiwear Agents	0.001-5	0.001-1.5
30	Seal Swellant	0.1-8	0.1-4
	Friction Modifiers	0.01-3	0.01-1.5
	Lubricating Base Oil	Balance	Balance

- When other additives are employed, it may be desirable, although not
- 35 necessary, to prepare additive concentrates comprising concentrated solutions or dispersions of the subject additives of this invention (in concentrate amounts hereinabove described), together with one or more of said other additives (said concentrate when constituting an additive mixture being referred to herein as an additive-package) whereby several additives can be added simultaneously to the
- 40 base oil to form the lubricating oil composition. Dissolution of the additive concentrate into the lubricating oil may be facilitated by solvents and by mixing accompanied with mild heating, but this is not essential. The concentrate or additive-package will typically be formulated to contain the additives in proper amounts to

provide the desired concentration in the final formulation when the additive-package is combined with a predetermined amount of base lubricant. Thus, the subject additives of the present invention can be added to small amounts of base oil or other compatible solvents along with other desirable additives to form additive-packages containing active ingredients in collective amounts of typically from 2.5 to 90%, and preferably from 15 to 75%, and most preferably from 25 to 60% by weight additives in the appropriate proportions with the remainder being base oil. The final formulations may employ typically 10 wt. % of the additive-package with the remainder being base oil. (All weight percents expressed herein, unless otherwise indicated, are based on active ingredient (A.I.) content of the additive, and/or upon the total weight of any additive-package, or formulation which will be the sum of the A.I. weight of each additive plus the weight of total oil or diluent).

Example 1 (Comparative)

In a three necked round bottom 250 ml flask, equipped with a magnetic stirrer, Teflon (PTFE) taps and rubber cap for the introduction of some of the reactants by a syringe, connected to a vacuum line, 0.73 g of 1-azido-1-methylethyl benzene were introduced followed by 100 ml of methylene dichloride. This solvent was previously dried by storage under vacuum after purification over phosphorous pentoxide. The reactor was pumped off and 12 ml of isobutylene, previously dried under calcium hydride, were condensed inside the flask. The reactor was then cooled down to -50°C, and 11 ml of a one molar solution of diethylaluminum chloride (DEAC) in heptane were introduced by a syringe through a rubber cap. The system was allowed to stand for 50 minutes and quenching was carried out by the introduction of 10 ml of methanol. The mixture was then treated with 100 ml of heptane filter to eliminate catalyst residues and concentrated. Polyisobutylene polymer (PIB) was collected by precipitation in acetone, filtered and dried under secondary vacuum to constant weight. The yield (7.2 g) was considered as complete and the polymer was analyzed by NMR and infrared spectroscopy and size exclusion chromatography (SEC). Using the peak at $2,100\text{ cm}^{-1}$ on the infrared spectrum characteristic of the azide group, and by comparison with the peaks at $1,475$, $1,390$ and $1,365\text{ cm}^{-1}$ characteristic of polyisobutylene and used as internal standard, and using the number average molecular weight ($M_n = 1600$) determined by size exclusion chromatography which was calibrated with known samples, an azide group functionality was found equal to 0.9 allowing to conclude that there is nearly one azide group per macromolecule. The polydispersity (M_w/M_n) index was found equal to 1.5. Using the NMR spectrum, the aromatic nuclei content of the polymer was determined and was found to correspond to 1,500 g of polymer per mole of aromatic nucleus. This resulted in the

calculation of an aromatic functionality of 1.07, supporting the conclusion that there was one aromatic nucleus per macromolecule within experimental accuracy. The monomer to initiator azido group ratio was $135/4.53 = 29.8$ is the degree of polymerization. The calculated molecular weight of the PIB plus end groups was
 5 1668 + 161 = 1829. The measured molecular weight was $\bar{M}_n = 1600$. The initiator azido group to catalyst molar ratio was calculated to be $-N_3:\text{catalyst} = 1:2.43$.

This example is provided for comparison with Examples 2 - 5. The initiator in Example 1 was 1-azido-1-methylethyl benzene, while that in Examples 2 - 5 was bis(1-azido-1-methylethyl)benzene. Additionally, Comparative Example 1 was carried
 10 out under such conditions that the molar ratio of Lewis acid to azide group was equal to 2.43, that is to say lower than 3. It shows that the number average molecular weight is close to, but lower than the theoretical one which could be calculated from the M:I molar ratio ($\bar{M}_n \text{ cal} = 1829$). The experimental molecular weight of 1,600 falls outside of the desired range. This example illustrates what is happening just above
 15 the upper limit of about 1:3 of the useful range for the ratio of pseudohalide group to Lewis acid, showing that the system begins to deviate from the apparently living behavior. Examples 2 - 5 below show the results when the molar ratio pseudohalide to Lewis acid group is within the desired range.

20 Examples 2-8

The technology of Example 1 was followed with the exceptions summarized in the following table:

25	Example(a)	Initiator		Reaction Diluent(c) (ml)	Monomer Amount(d) (m mole)	Catalyst(e) (m mole)
		Type(b)	Amount (m mole)			
	1	AMB	6.08	100	134	11
	2	bis AMB	2.2	"	60	18
30	3	"	2.2	"	90	18
	4	"	2.2	"	160	18
	5	"	2.2	"	215	18
	6	"	1.0	"	103	6
	7	"	4.3	80	103	9.4
35	8	"	0.196	90	84	1.5

(a) Examples 1 and 8 used a 250 ml. round bottom flask; Examples 2-7 a 250 ml. double walled reactor.

- (b) AMB = 1-azido-1-methylethyl benzene
 bisAMB = bis(1-azido-1-methylethyl) benzene
 (c) methylene dichloride
 (d) isobutylene
 5 (e) diethylaluminum chloride (1M in heptane) in Examples 1-5, 8; TiCl_4 in Example 6; BCl_3 (1M in methylene dichloride) in Example 7.

The results of the Examples 1 - 9 are summarized on Table 1, with "M" being moles of monomer, "I" moles of initiator, "Cat." moles of catalyst, " $-\text{N}_3$ " moles of azide functional group, "Mn cal'd" calculated number average molecular weight, "Mn meas." measured number average molecular weight, " Δ Mn" the difference between "Mn cal'd" and "Mn meas.", and "MWD" molecular weight distribution (polydispersity index). The calculated or theoretical molecular weight, Mn cal'd, was determined from the molar ratio of initial monomer concentration "Mo" to initial initiator concentration "Io" plus the molecular weight of initiator "I". (Mn cal'd = $\text{Mo}/\text{Io} + \text{I}$).

Table 1

Ex.	M/I	I/CAT	$-\text{N}_3/\text{CAT}$	Mn			%	MWD	Functionality [‡]	
				cal'd.	meas.	Δ			Azide	Aromatic
1*	29.8	1/2.43	1/2.43	1829	1600	229	12.5	1.5	0.9	1.07
2	27.27	1/8.18	1/4.09	1771	1650	121	6.8	1.3	2.0	1.09
3	40.90	1/8.18	1/4.09	2535	2350	185	7.2	1.3	2.1	1.08
4	72.73	1/8.18	1/4.09	4317	4250	67	1.6	1.2	2.1	0.95
25 5	97.73	1/8.18	1/4.09	5717	5420	267	4.7	1.3	2.1	0.94
6*	103.0	1/6	1/3	6012	5300	712	11.8	1.7	1.7	0.95
7*	24.0	1/2.19	1/1.10	1585	2100	515	32.5	1.8	2.1	—
8	442	1/7.89	1/3.95	25001	24300	701	2.8	1.3	2.0	1.0
9(I)	50.0	1/7.73	1/3.86	3044	3050	6	0.2	1.3	2.0	1.0
30 9(II)	—	—	—	4040	4062	22	0.5	1.4	2.0	1.0

* Comparative Examples

[‡] per molecule

35 Example 9

A three necked round bottom 250 ml flask, equipped with a magnetic stirrer and small graduated capillary tubes for the handling of small quantities of isobutylene, Teflon taps and rubber cap for the introduction of some of the reactants by a syringe, was connected to a vacuum line. The reactor was then flushed with dry
 40 nitrogen and 0.053 g of bis-1,4-(1-azido-1-methylethyl)benzene were introduced, followed by approximately 97 ml of methylene dichloride which solvent was previously dried by distillation over phosphorous pentoxide and stored under vacuum before

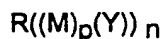
use. The reactor was rapidly pumped off and 1.0 ml of isobutylene, previously dried under calcium hydride, was condensed inside the flask. The reactor was cooled to -50°C, and 1.7 ml of DEAC (1M in heptane) were introduced by a syringe through a rubber cap. Thus, the isobutene concentration was 0.11 mole/l, the concentration of
5 initiator was 2.2×10^{-3} mole/l and the DEAC was 1.7×10^{-2} mole/l. Accordingly, the molar ratio Lewis acid/azide group was 3.86. The system was allowed to stand for 50 minutes before the sampling of approximately 10 ml of the reaction medium. Quenching of the sample was carried out by the introduction of 1 ml of methanol. The resulting mixture was discarded for further analysis.

10 After sampling, a new charge of 0.32 ml of isobutylene was added in the reactor kept at -50°C. The concentration of monomer units (previous polymer + new charge) was then 0.15 mole/l. The system was allowed to stand at -50°C for a new period of 50 minutes and quenched. The sample was then treated by 10 ml of heptane filtrated to eliminate catalyst residues and concentrated. The final polymer,
15 containing the polymer produced after the introduction of the second charge of monomer, was collected by precipitation in acetone, filtrated and dried under secondary vacuum to constant weight. The yield was considered as complete and the polymer was analysed by NMR and infrared spectroscopy and size exclusion chromatography (SEC).

20 The number average molecular weight (M_n) was 3,050 for the initial sample, and $M_n = 4,062$ for the final polymer, was determined by size exclusion chromatography which was calibrated with known samples. This was compared with the theoretical calculated molecular weight determined based on the molar monomer to diazide ratio ($M_n = 3,044$ and 4,440) respectively for the sample and the main
25 polymer). The subsequent polymerization agreement between the measured and calculated molecular weights shows living polymeric behavior. Using the peak at $2,100 \text{ cm}^{-1}$ on the infrared spectrum characteristic of the azide group, and by comparison with the peaks at 1,475, 1,390 and $1,365 \text{ cm}^{-1}$ characteristic of polyisobutylene and used as internal standard, an azide group functionality was
30 found equal to 2.0 for both samples, indicating that there are two azide groups per macromolecule. The polydispersity index was found equal to 1.3 and 1.4 respectively for the initial sample and the final polymer. On the NMR spectrum, the aromatic nuclei content of the polymers was determined and was found to correspond to one aromatic nucleus per macromolecule within experimental accuracy. This incremental
35 monomer addition technique was carried out within the useful range for the molar ratio of 3.86 of Lewis acid to pseudohalide group. This example demonstrates the apparently living character of the system since the addition of monomer resulted in continuing polymerization.

CLAIMS:

1. A method for the direct synthesis of polymeric materials functionalized with nitrogen-containing functional groups, comprising the steps of providing a cationically polymerizable monomer, and initiating polymerization by the addition of a cationic polymerization catalyst, in the presence of a nitrogen-containing initiator compound having at least one nitrogen-containing functional group selected from -N₃, -NCO, -OCN, -SCN, -CN and -NCS chemically bound to a release moiety, wherein the ratio of moles of catalyst to nitrogen-containing functional groups is greater than 3:1.
2. The method according to claim 1 wherein the cationic polymerization catalyst is a Friedel-Crafts catalyst which is mixed with the nitrogen-containing initiator compound and then contacted with the polymerizable monomer to initiate polymerization, and wherein the ratio of moles of catalyst to nitrogen-containing functional groups is greater than 4:1.
3. The method according to claim 1 or claim 2 wherein said nitrogen-containing functional group is covalently bound to a tertiary or secondary carbon of said release moiety.
4. The method according to any of claims 1 to 3 wherein said release moiety is resonance stabilized allylic, benzylic, or tertiary aliphatic moiety.
5. The method of claim 1 wherein said nitrogen-containing initiator is hydrazoic acid or bis(1-azido-1-methylethyl)benzene.
6. The method according to any of claims 1 to 5 wherein the monomer is isobutylene.
7. The method according to any of claims 1 to 6 wherein the polymerization is conducted at a temperature of from -80°C to -20°C.
8. A polymer composition having the formula:



wherein

R is selected from at least one group consisting of hydrogen, a hydrocarbyl group, and a hydrocarbyl-substituted group;

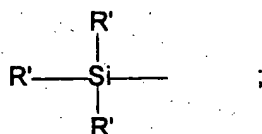
Y is selected from at least one group consisting of an azido, cyano, carbonylamino, thiocarbonylamino, cyanato, and thiocyanato;

M is at least one repeat unit derived from a cationically polymerizable monomer;

p is an integer greater than one; and

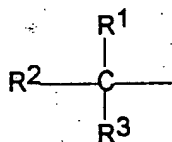
n is an integer of at least one.

9. The polymer composition according to claim 8 wherein R is: alkyl of from 3 to 100 carbon atoms; aryl of from 6 to 20 carbon atoms; alkaryl and aralkyl of from 7 to 100 carbon atoms; cycloaliphatic of from 3 to 20 carbon atoms; a hydrocarbyl substituted silyl group of the formula:



wherein each R' is the same or different and is hydrocarbyl;

a substituted methyl group of the formula:

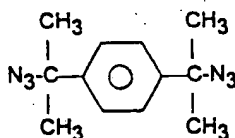


wherein R¹, R² and R³ are the same or different and are hydrogen, alkyl, aryl, alkaryl, aralkyl, heterocyclic or cycloalkyl with the proviso that no more than one of R¹, R² and R³ is hydrogen; $\emptyset\text{CH}_2$ -; $\text{CH}_3\emptyset\text{CH}_2$ -; $\text{C}_2\text{H}_5\emptyset$ -; $\text{CH}_3\emptyset$ -; and $(\text{CH}_3)_2\emptyset$ -.

10. A functionalized polymer comprising the polymeric material prepared by the method of any of claims 1 to 7 or polymer composition according to claim 8 or claim 9 wherein the nitrogen containing functional group is further reacted to form a functional group selected from carboxyl groups, cyanate groups, amine groups, hydroxyl groups, triazole groups, nitrile groups, nitrene groups and dimerized nitrene groups.

11. A derivatized polymer comprising the reaction product of at least one functionalized polymer of claim 10 and a derivatizing compound selected from amines, alcohols and metal salts.

12. A compound having the formula:



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A. CLASSIFICATION OF SUBJECT MATTER IPC 5 C08F2/38 C08F4/00 C08F8/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 5 C08F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 349 195 (EXXON CHEMICAL PATENTS INC.) 3 January 1990 see page 5, line 15 - line 54 see page 7, line 17 - line 55 see page 9, line 6 - line 51 see page 10, line 32 - line 54; claims 1-20	8,9,12
X	& US,A,5 032 653 cited in the application	8,9,12
A	EP,A,0 265 053 (KENNEDY, JOSEPH PAUL) 27 April 1988 see claims 1-10 --- -/--	1
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "Z" document member of the same patent family		
Date of the actual completion of the international search 19 April 1994		Date of mailing of the international search report 29. 04. 94
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016		Authorized officer Permentier, W

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>CHEMICAL ABSTRACTS, vol. 117, no. 1, 13 July 1992, Columbus, Ohio, US; abstract no. 8706q, KUZNETSOVA, M. B. 'MANUFACTURE OF POLYISOBUTYLENE IN PRESENCE OF CHAIN-TRANSFER AGENTS' page 15 ; see abstract & SU,A,1 659 424 (KAZAN CHEMICAL-TECHNOLOGICAL INSTITUTE) 30 June 1991</p> <p>-----</p>	1

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Information on patent family members

international application no.

PCT/US 93/11918

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0349195	03-01-90	US-A- 5032653 JP-A- 2084403	16-07-91 26-03-90
US-A-5032653	16-07-91	EP-A- 0349195 JP-A- 2084403	03-01-90 26-03-90
EP-A-0265053	27-04-88	JP-A- 1062308 US-A- 4929683 US-A- 5066730	08-03-89 29-05-90 19-11-91
SU-A-1659424	30-06-91	NONE	